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14. ABSTRACT The PI has developed several design approaches for the creation and investigation of organic macromolecules with large 2PA cross-sections important to the goals of the Air Force for optical limiting and sensor applications. The PI's research laboratory has investigated the critical issues in novel macromolecular systems concerning excitation localization and delocalization, disorder and rigidity as well as the role of through space interactions and quinoidal character contribution in these systems. We have also investigated the intersystem crossing process in Pt-acetylide complexes in a broad range of temperatures 4.2K-294K. Utilizing the quantum size effects in novel gold and silver nanoclusters will lead to cheap and efficient optical limiters as well as to the development of new generation of two-photon probes for imaging applications. We continued the systematic investigation of the extraordinary nonlinear optical properties and femtosecond optical excitation dynamics in large oligomeric macromolecules possessing a macrocyclic topology. For these systems we have demonstrated superior two-photon cross-sections per unit molecular weight with very small linear absorption in the transparency window. It paves the way to development of highly concentrated and inexpensive optical limiting materials.			
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Mechanistic Investigations of Organic Aggregates with Different Topologies for Optical Limiting Applications

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Recently the PI has developed several design approaches for the creation and investigation of organic macromolecules with large 2PA cross-sections important to the goals of the Air Force for optical limiting and sensor applications. The new materials and subsequent measurements provided valuable information regarding the optimization and discovery of novel NLO materials with enhanced properties. We have also probed in detail the mechanism of the excitations and time-scales of optical and electronic events in these novel materials. The PI's research laboratory has investigated the critical issues in novel macromolecular systems concerning excitation localization and delocalization, disorder and rigidity as well as the role of through space interactions and quinoidal character contribution in these systems.¹⁻²⁰ Measurements with these materials have been carried out in conjunction with the design and fabrication of new quinoidal oligothiophenes,¹¹⁻¹³ circular molecular systems,²⁻⁸ Fe-, Ru-,⁸ Pt- complexes,^{19,20} and small metal nanoparticle systems²¹⁻²⁴ as to provide a direct feed back to the understanding of the structure/function relationships. Due to biradical character of the ground state for quinoidal oligomers these systems open new avenue in the design of highly responsive optical limiting materials covering very broad spectral range up to 2200nm.¹² Novel low bandgap quinoidal oligothiophenes demonstrated broad absorption spectrum and strong two- and three-photon absorption responses.^{12,13} We have also investigated the intersystem crossing process in Pt-acetylide complexes in a broad range of temperatures 4.2K-294K.¹⁹ This investigation showed minor involvement of conformational changes in the intersystem crossing process resulting in important structure-property relationships allowing for building more efficient optical limiters. We continue the systematic investigation of the extraordinary nonlinear optical properties and femtosecond optical excitation dynamics in large oligomeric macromolecules possessing a macrocyclic topology.²⁻⁸ For these systems we have demonstrated superior two-photon cross-sections per unit molecular weight up to 31GM/(unit molecular weight) with very small linear absorption in the transparency window. It paves

the way to development of highly concentrated and inexpensive optical limiting materials.

Our previous experiments in monolayer protected small gold clusters demonstrated extremely high two-photon cross section values per one gold atom ($\sim 17,000 \text{ GM/atom}$).²¹ Utilizing the quantum size effects in novel gold and silver nanoclusters will lead to cheap and efficient optical limiters as well as to the development of new generation of two-photon probes for imaging applications.²¹⁻²⁴

Novel cubic 3-D systems based on octasilsesquioxanes investigated in my lab demonstrated strong enhancement in two-photon absorption cross-section as compared to single stilbene building block (corner).^{14,25} This result opens the way to the development real 3-D building blocks which are capable of forming highly dense three-dimensional structures with strong nonlinear optical absorption.¹⁴

A. Initial results on nonlinear optical properties of quinoidal oligothiophenes – novel approach to greatly enhanced nonlinear absorbers

We have initiated the investigation of nonlinear optical properties of novel quinoidal oligothiophene systems possessing biradical character of the ground state.^{12,13} Quinoidal oligothiophenes possess positionally locked double bonding between repeat units giving a forced degree of π -overlap and high rigidity lacking in traditional oligomers.^{13,26,27} Highly planar quinoidal structures with extended conjugation, low bandgap, and amphoteric redox behavior have received great attention in the field of organic electronics.²⁶⁻²⁸ We showed that in addition to those electronic transport properties quinoidal oligothiophenes demonstrate remarkable nonlinear absorption properties in a very broad spectral range.^{12,13} Recent theoretical studies predicted that open-shell systems can demonstrate very strong enhancement of NLO susceptibilities as compared to the traditional closed-shell configurations.²⁹⁻³¹ We showed that quinoidal oligothiophenes possessing biradical character of the ground state demonstrate remarkable and strong nonlinear absorption properties in a very broad spectral range.¹² While structurally some quinoidal oligomers (QOTs) resemble “traditional” D- π -D motif already proved beneficial for nonlinear absorption³²⁻³⁴ they are physically very different

as compared to aromatic oligomers (OTs) which is clearly indicated by the unusually broad absorption spectrum extending to the IR region even for short oligomers.^{12,13,26,27}

Detailed here is the use of NIR femtosecond pulsed excitation to drive three-photon absorption (3PA) in a cyano-terminated quinoidal oligothiophene (QOT) dimer to the exclusion of all other fluorescing processes, resulting in 3PA emission bright enough to be visible by eye. Through steady state, multiphoton and ultrafast transient spectroscopy it is shown that despite competing nonlinear optical processes, such as an available two-photon transition (2PA) and excited state absorption (ESA), emission characteristics remain an I^3 process explicitly due to 3PA. Specifically, we have shown the viability of a two photon transition at the pump wavelength, strong excited state 3 absorption, and display neither occurs to a significant degree in this QOT system when pump energies match both a virtual state near resonant with a viable 2PA state and a higher lying 3PA energy level. This study provided a clear method for evaluating multiband 3PA emitters which bypasses much of the ambiguity observed in purely absorption based studies where 2PA, ESA and 3PA may all contribute to signal and are difficult to distinguish. Additionally, this study has introduced a rigid, molecular wire-like thiophene oligomer as a strong nonlinear optical responsive material with gross response changes based on small changes in IR excitation.

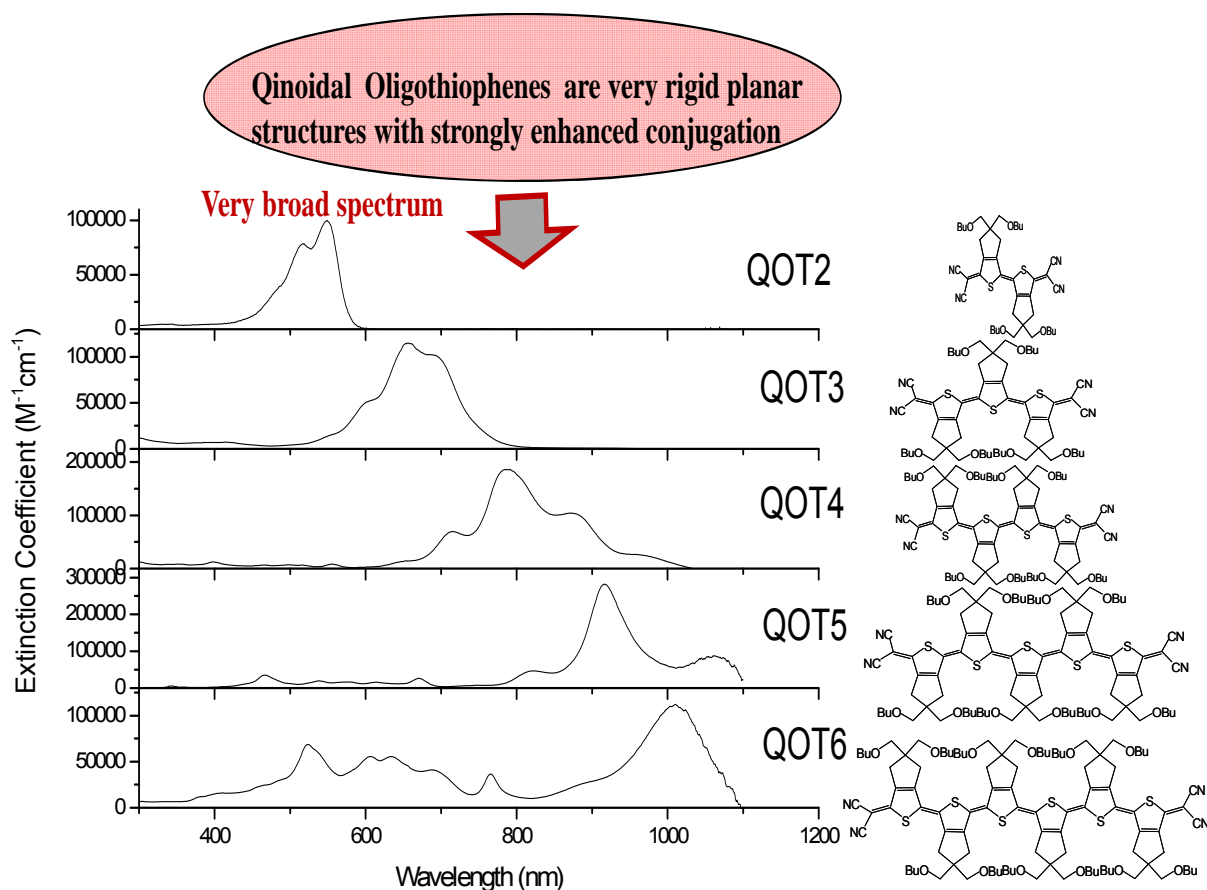


Figure 1. Absorption spectra and chemical structures of quinoidal oligothiophenes investigated in PI's laboratory.

Highly planar quinoidal structures with extended conjugation demonstrated very broad absorption spectra extending to the NIR for longer oligomers. Figure 1 shows the steady-state absorption spectra of quinoidal oligothiophene (QOT) arrays in THF as well as the molecular structure of each oligomer. With increasing chain length, the absorption red shift of the main band (the most intense bands in each spectrum) is clearly seen. This continuous red shift shows that the pi-electron delocalization is efficient in QOTs. A critical observation can be made by comparing the absorption spectra of our QOT arrays to those of oligothiophene (OT) arrays connected with a single bond between thiophene units.³⁵ In the QOT arrays, the absorption spectra show continuous redshift with the increasing number of thiophene units, while OT arrays show saturation behavior at 560 nm. This is depicted in Figure 2, where molecular conjugation length is

compared to π - π^* electronic absorption band maxima.¹³ This optical behavior, close to linear with regards to the unit number, in the QOT arrays indicates efficient delocalization of π -electron conjugation, while the saturation behavior in the OTs show increasingly less efficient π -electron delocalization in the longer arrays.¹³ This provides clear evidence that QOT is an extremely promising species for molecular wire type behavior and viable for a number of applications where strong NIR response is also needed.

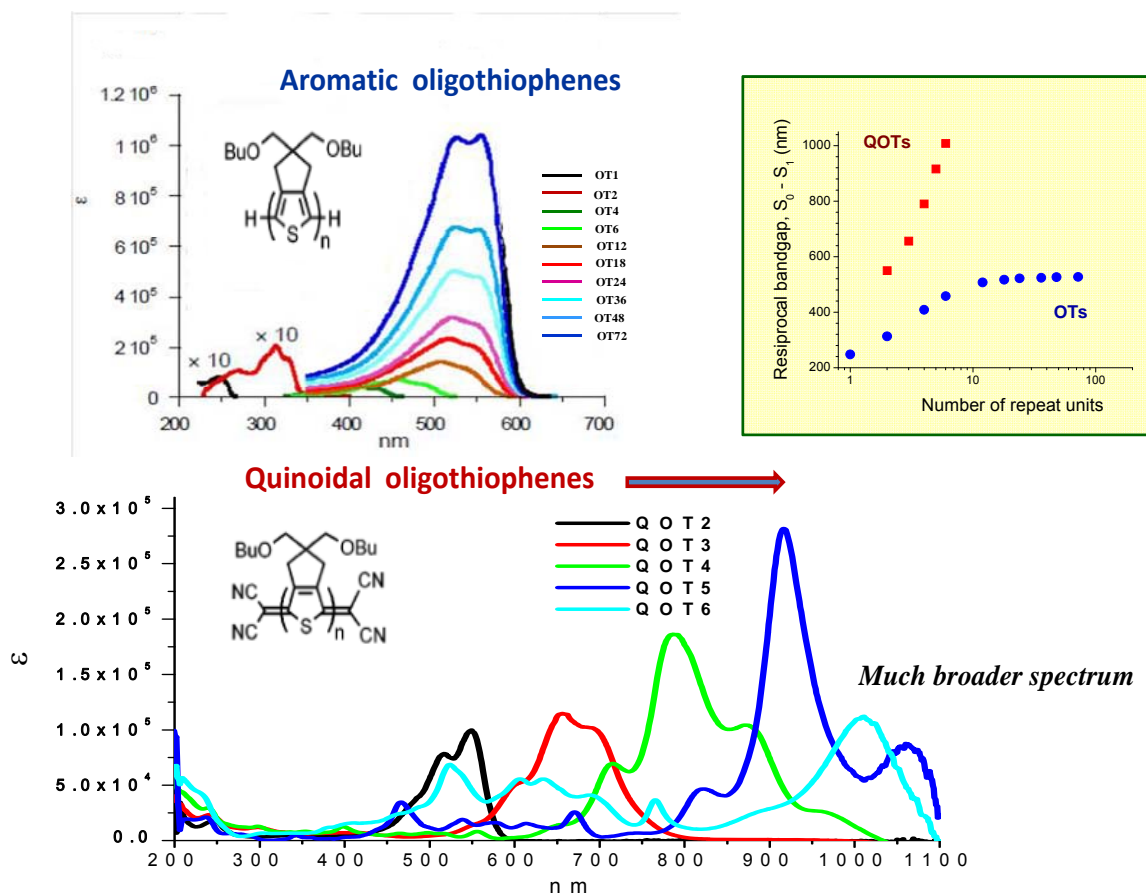


Figure 2. Quinoidal OTS vs aromatic (traditional) OTs: In QOTs absorption spectra show continuous red-shift with increasing number of thiophene units while OT show a saturation behavior.

Being intrinsically more rigid than OT, QOT may also be more suitable for highly ordered solid state devices.

We have investigated nonlinear absorption properties of quinoidal oligothiophenes and discovered a co- existence of strong three-photon and two-photon absorption in the same molecule. The power dependence of the emission undoubtedly showed that the cubic low characteristic of three-photon absorption takes over the lower order nonlinearities and certainly dominates the nonlinear absorption process in this spectral region (Figure 3).¹²

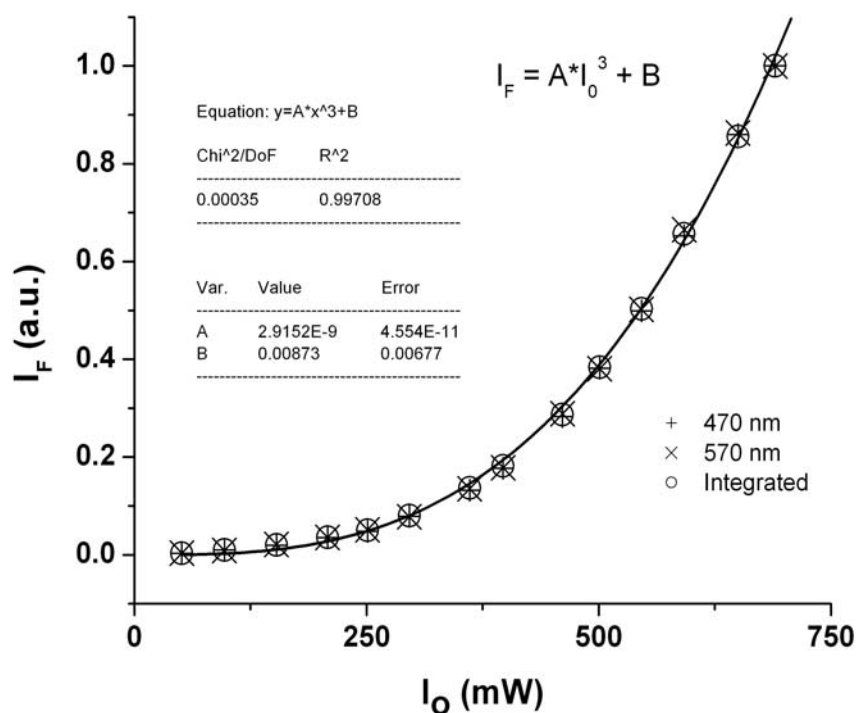


Figure 3. Efficient 3-Photon Absorption process in quinoidal thiophene dimer.

In spectral regions around 700nm and 900nm two-photon absorption is the dominating nonlinear transmission mechanism in the same molecule (Figure 4, right).¹² Polynomial fitting of the fluorescence intensities for fluorescence features and integrated peak intensity are presented in Figure 3 . Also shown is the LOG(I_F)- LOG(I_0) plot depicting a

slope of three with increasing excitation power, indicating a I^3 dependence typical of three-photon excitation (Figure 4, left).

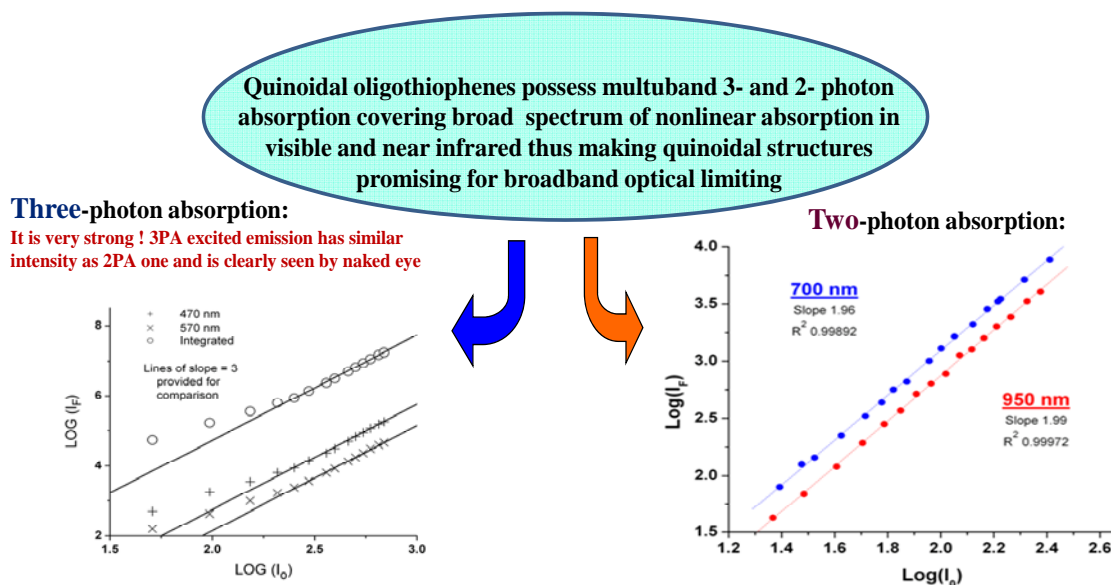


Figure 4. Multiband two- and three- photon absorption processes in QOT2.⁵³

Enhanced 2PA processes have been observed in multiband oligomeric systems where the presence of an intermediate state near the induced virtual state provides resonance energy matching and leads to a greatly enhanced cross-section when compared to similar systems without a mediating state.³⁶ We proposed that the presence of a relatively pure 3PA emission signal, despite the strong possibility of a highly responsive two-photon band at 415 nm, can be explained by a regime similar to the intermediate band stabilization in a two-photon process. By choosing an excitation regime which provides two-photon energy matching to the 415 nm excitation band and one-photon energy matching to the 415 nm - 265 nm transition, 3PA to the 265 nm band can be achieved by a near resonant two-photon virtual state being promoted to the 3PA state in the presence of a strong 800 nm flux. We compare this to our one-photon excitation regime. It is important to note that the strong coupling of the $\frac{2}{3} \Delta E$ virtual state to the 415 nm band provides a different regime for multiphoton emission than that observed in 1PA emission. We proposed that the virtual state coupling to an excited state having

biradical character allows for a degree of biradical character in the 3PA state, very different from the 1P case. This is supported by a normalized polynomial that shows in Figure 4 the same power dependence for all emission features, indicating that both emission features derive from the same 3PA excited state despite differing relaxation pathways. Excitation at energies which did not target both the 3PA enhancing 425 nm energy level and the 265 nm target state (off resonance excitation) showed only a single emission type and quadratic power dependence.

In combination with very broad absorption coverage the co-existence of strong three-photon and two-photon absorption in the same molecule of the quinoidal oligomer opens a new avenue to creation of extremely broad band nonlinear absorbers and limiters utilizing only few oligomers or even one quinoidal oligomer.

**Quinoidal Oligomer demonstrated very high molecular 3-photon
absorption cross- section in comparison with other systems -
 $10^{-74}\text{cm}^6\text{s}^2\text{phot}^{-2}$**

1. CdSe/CdS nanorods, *J. Phys. Chem. C*, **2011**, *115*, 17711,
 $\sigma_3 = 1.5 \times 10^{-75} \text{cm}^6\text{s}^2\text{phot}^{-2}$
2. Porphyrin dimers, *Chem. Comm.* **2010**, 46, 2121,
 $\sigma_3 = 7.6 \times 10^{-76} \text{cm}^6\text{s}^2\text{phot}^{-2}$
3. Fluorene-based oligomers, *Chem. Eur. J.*, **2009**, *15*, 11681
 $\sigma_3 = 3.6 \times 10^{-77} \text{cm}^6\text{s}^2\text{phot}^{-2}$
4. Organometallic Dendrimers, *Ang.Chem. Int.Ed.* **2007**, *46*, 731
 $\sigma_3 = 1.5 \times 10^{-77} \text{cm}^6\text{s}^2\text{phot}^{-2}$
5. BDPADSB dendrimer, *J. Lumin.* **2007**, *127*, 28
 $\sigma_3 = 1.5 \times 10^{-79} \text{cm}^6\text{s}^2\text{phot}^{-2}$

Figure 5. 3-photon absorption cross-section of QOT2 in comparison with other efficient 3-photon absorbers³⁷⁻⁴¹

Three-photon absorption cross- section is exceptionally strong for this organic molecule: $10^{-74} \text{cm}^6\text{s}^2\text{phot}^{-2}$. It is higher than those for best performing inorganic quantum dots 3-photon absorbers⁶ and 2 orders of magnitude higher than those for organic conjugated systems (Figure 5).³⁷⁻⁴¹

The mechanism of very strong three-photon absorption is associated with 2-photon absorption mediation promoting efficient absorption of the third photon. New and unusual is the dominance of three photon absorption over two-photon absorption in the area, possibly, due to specific structure of intermediate states (Figure 6).¹²

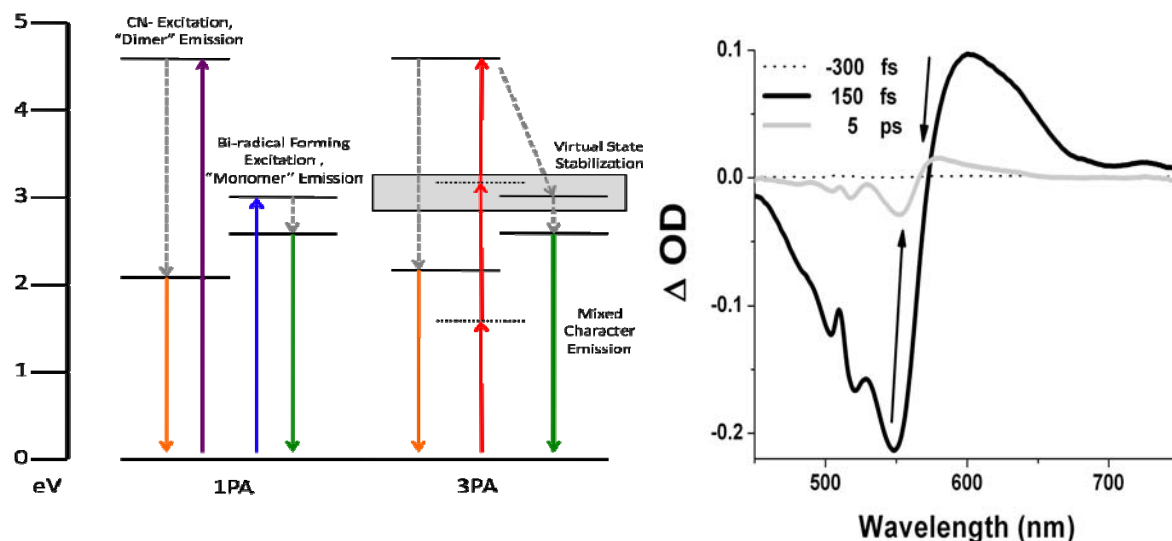
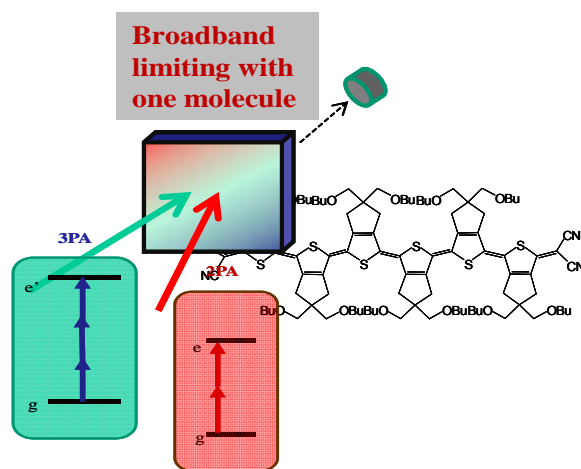


Figure 6. One and Three-Photon energy diagram depicting 2PA-mediated 3PA and subsequent emission for QOT2(left); transient absorption data supporting virtual state enhancement mechanism of 3PA (right, see text).

Transient absorption study showed that the observed 3PA cannot be a formal 2PA process followed immediately by excited state absorption.¹² 3PA process is ultrafast, more complex in nature. Kinetic traces (Figure 6, right) show 2 ps lifetimes from both regions, with comparable amplitudes and long time scale residuals. Comparing the ratio of peak integrations, $\int (\text{ESA})d\text{eV} / \int (\text{PB})d\text{eV}$, gives similarly high ratios during the primary kinetic lifetime (0.61 at 150 fs) and after the majority of relaxation (0.58 at 5 ps) which is an indication of ESA intrinsically linked to PB population density. Without implicitly determining the ESA cross-section, these results display clear ESA to the 265 nm energy level in our QOT2 system after excitation while integration provides additional confirmation of an extremely high rate of ESA which remains during the entirety of the excited state lifetime. While this study illuminates the types of interconversion that are allowed in our QOT system, it is critical to note that the observed 3PA cannot be a formal 2PA process followed immediately by ESA. At the intensities observed during the pulse (~ 5 nJ focused onto a diffraction limited point), where all light is at a wavelength appropriate for ESA to occur, $\langle P_{\text{ESA}} \rangle$ approaches unity and the resultant fluorescence signal would be a function of I^2 . Additionally, at lower excitation intensities below the threshold of observable 3PA emission, a formal 2PA excited state would have emission characteristics which mimic those observed in the 1PA 415 nm excitation regime and is also unobserved. These findings also provide a good argument for the use of 3PEF (three photon excited fluorescence) as an appropriate technique for materials investigations where absorption studies alone would have a large degree of ambiguity regarding the source of observed nonlinearities. It proceeds through the virtual 2PA state.¹² This is an important finding allowing building novel broadband nonlinear absorbers utilizing both two-photon and enhanced three photon absorption in one material.



Impact:

- Novel quinoidal oligomers utilize various **multiphoton nonlinear processes in one macromolecule**.
- Monomolecular, very homogeneous **broadband nonlinear absorbers** and **optical limiters** can be created on the base of quinoidal structures.
- These structures possess **remarkable processability** and are inexpensive.
- Broadband quinoidal structures have also important applications in **photovoltaics** (better match to sunlight spectrum), organic **photodetectors** (in NIR), and **organic electronics** (ambipolar carriers response)

A. Enhancement of Two-Photon Absorption Cross Section in Giant Cyclic Oligomers with Tunable Size

We have systematically investigated a series of organic oligomers in a new, circular geometry (Figure 6).^{2,3,5,6,42,43} The circular geometry presents us with the possibility of complete conjugation. Linear macromolecules have defects which hinder conjugation over the entire chain. This seems less likely in case of circular chromophores since there are no “end-effects”.⁴⁴

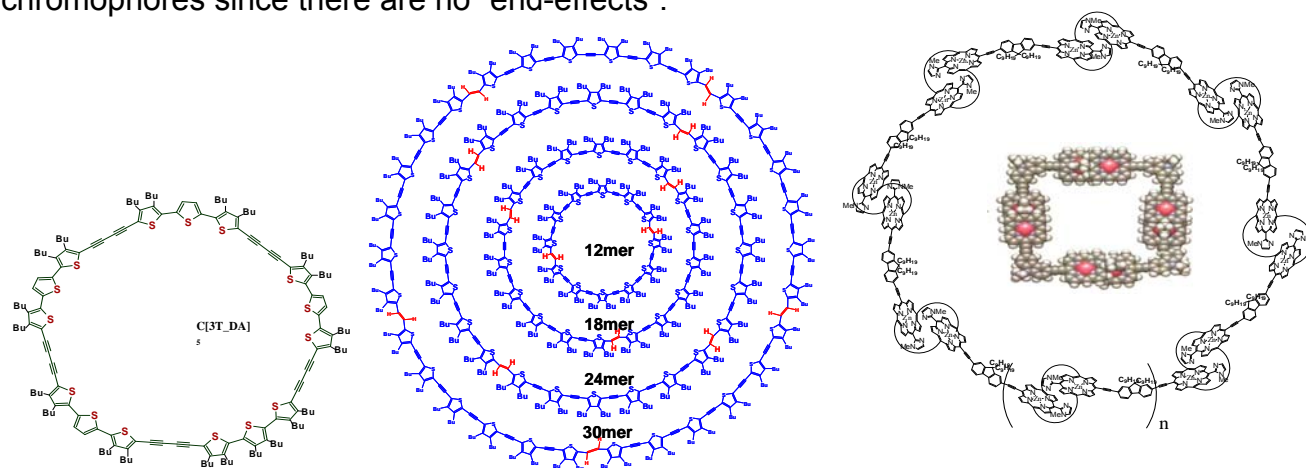


Figure 7. Structures of the cyclic thiophenes and porphyrins studied in this investigation.^{2,3,5,6}

We have studied the nonlinear optical properties of macrocyclic thiophenes and porphyrins (Figure 7).^{2,3,5,6} Their TPA cross section (δ) spectra were measured using two-photon excited fluorescence (TPEF) method. We have also investigated the fluorescence dynamics and the excited state dynamics in these chromophores. These

systems are equally interesting from a theoretical standpoint. TPA results showed a 550% enhancement in the TPA cross section of a single C[3T_DA]₂ unit upon increasing the ring size.⁵

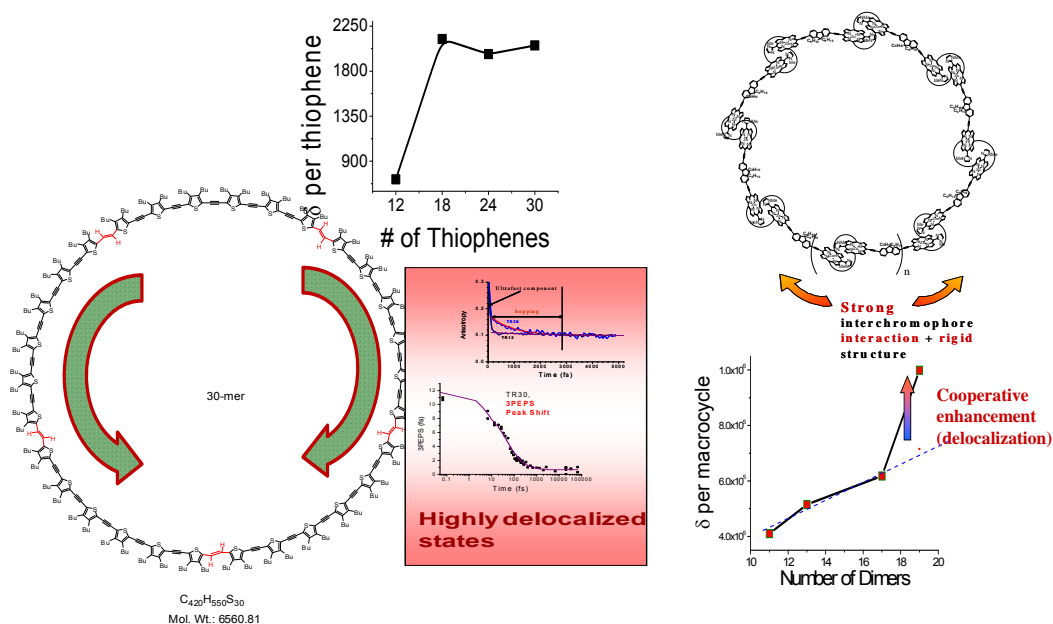


Figure 8 . Important role of highly delocalized states in nonlinear optical response enhancement of giant macrocyclic systems.^{2,3,5,6}

Femtosecond fluorescence upconversion measurements have shown the presence of coherent energy transfer in macrocycles, resulting in complete delocalization of the excitation over the major portion of the ring even for giant macrocycles (Figure 8).^{2,3,5}

Recently, molecules with excellent two photon absorption (2PA) properties, which employ a combination of the large π -conjugation found in porphyrins and acetylene linkages which provide a pathway for electronic communication between porphyrin units, have been reported. 2,7-Fluorene provides an angle of 160° between two porphyrins and can be expected to allow formation of large, very stable macrorings based on complementary coordination of imidazolyl to zinc. These structures are interesting from the viewpoint of 2PA enhancement as well as for optical limiting materials, because fluorene is known to be a good π -spacer for such materials.⁴⁵⁻⁴⁸

Based on these considerations, we designed the new fluorene-bridged bis(imidazolylporphyrin), in which an acetylene bond is employed to allow π -conjugation between chromophores (Figure 9), with the expectation that extremely large macrocyclic arrays (3R) would form through self-organization, with the most stable cyclic structure being the 18-mer ($n = 8$, 36 porphyrins).

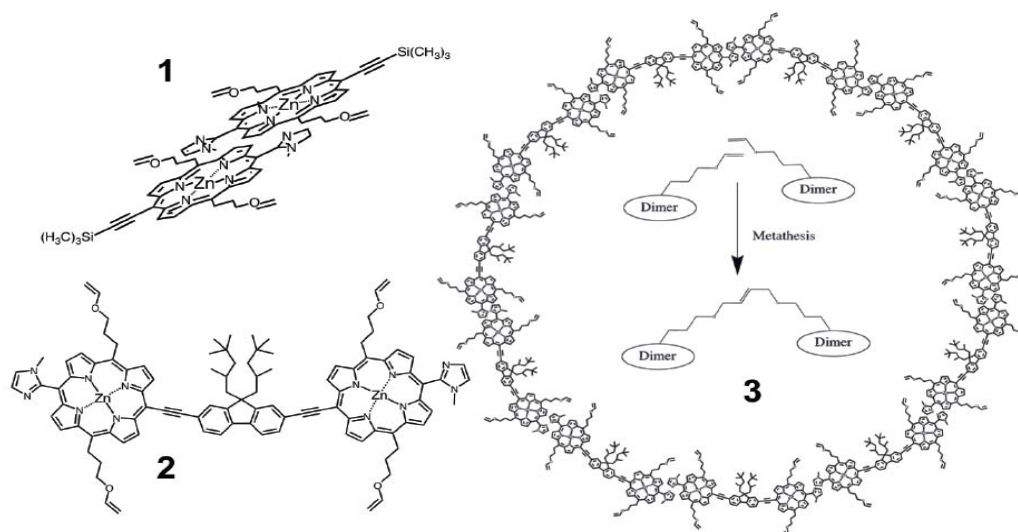


Figure 9. Self-assembling process of the giant porphyrin macrocycle formation.

The macrocycle form was sought implicitly for the TPA enhancement seen in other hyperconjugated systems, such as cyclic thiophenes. In addition, the excited state absorption characteristics of porphyrins are in such a way that they provide very good avenues for reverse saturable absorption both for short pulse-width as well as long pulse-width regimes.

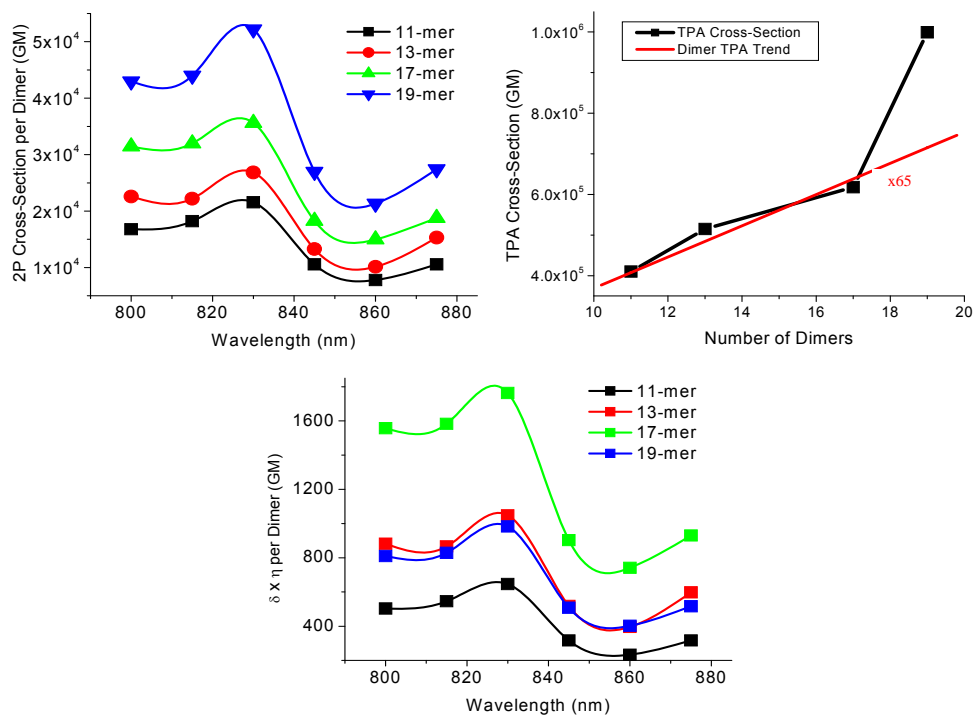


Figure 10. Trends in two-photon absorption for porphyrin macrocycles.

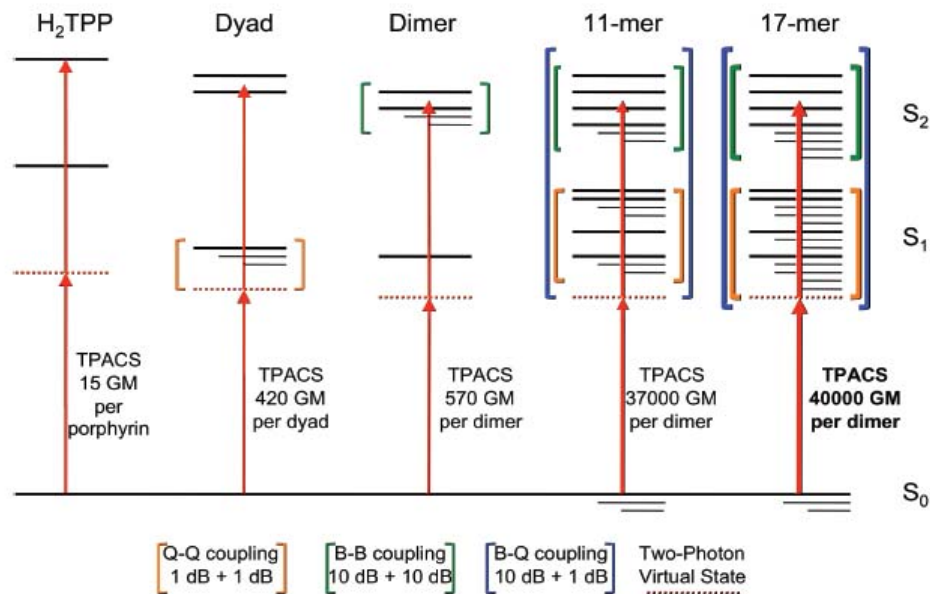


Figure 11. Energy level structure and relaxation pathways for porphyrin macrocycles

These investigations set an important structure-property relationship connecting highly delocalized states in macrocycles with strong enhancement of two-photon responses

(Figure 10). Record high TPA –absorption cross-sections per unit molecular weight for organics have been obtained in giant cyclic oligomers in this work (Figure 12)^{3,5,6}

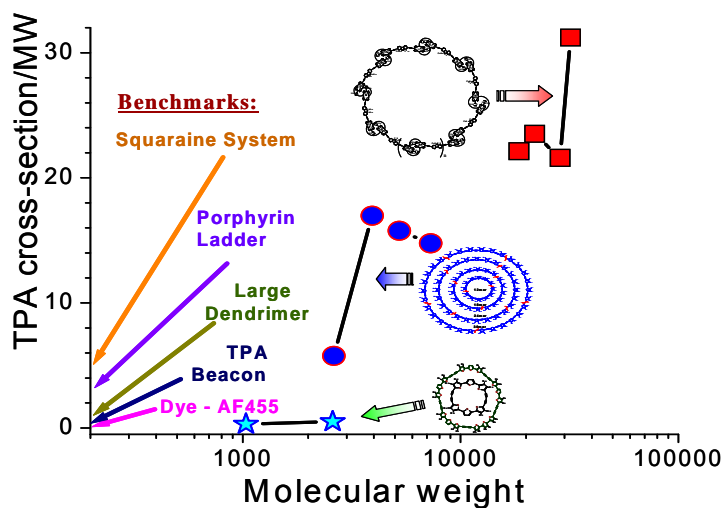


Figure 12. Two-photon absorption cross-section per unit molecular weight for macrocycles as compared to other systems possessing large two-photon response.

Impact:

Rigid ordered structure and highly delocalized optical excitations provide **extremely high TPA-cross-sections** for the macrocycles.

Porphyrin-based macrocyclic systems demonstrated record high TPA-cross-section of **~30GM per unit molecular weight** providing the basis for an **inexpensive ultrafast optical limiting system**.

Ordered structural organization leads to a **very low linear absorption** (<0.5%) for weak light even for highly concentrated thiophene-based samples which makes these systems very important for optical limiting applications with **ultrafast response**.

New thiophene-based **cyclic light harvesting antenna** is of great importance for new generation of thiophene-based efficient photovoltaic systems

Ultra-Fast Exciton Dynamics in the Platinum Acetylide Complex at Low Temperature

Platinum acetylides represent a class of organometallic structures whose nonlinear optical properties have received considerable attention for their possible application in OLEDs, photovoltaics, optical power limiters, and other optical devices. Interest in these structures stems from the material's ability to couple two electronic states with

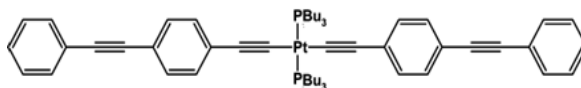
different spin multiplicity.⁴⁹⁻⁵¹ Specifically, the platinum atom generates strong spin-orbit coupling (heavy atom effect) allowing for ultra-fast intersystem crossing (ISC) or, in the opposite route, the ability for singlet and triplet electron-hole pairs to recombine emissively. Furthermore, the platinum d-orbitals conjugated with the ligand π -orbitals allow for charge migration across the oligomers.⁴⁹ For these reasons and that the platinum acetylides are easily synthesized, highly emissive, and robust they make exciting systems for numerous applications and also as model systems to study spectroscopically.

Recent work has been on determining the excited state phenomena like excited state absorption (ESA), triplet state absorption spectrum (TTA), two-photon absorption, excimers, phosphorescence, ISC and the spatial extent of the excited states.²⁰ We have shown that the ISC for the PT1 structure is less than 100fs and that the time constant increases with increasing the chain length.²⁰ The symmetry breaking that occurs to localize the triplet state on one of the ligands has received considerable interest in terms of transport properties of triplet excitons also important for applications.

Time resolved infrared spectroscopy has been used to study the symmetry properties of the ground state and lowest excited triplet state of $[\text{Pt}(\text{P}^n\text{Bu}_3)_2(\text{ethynylbenzene})_2]$ by Emmert et al.⁵² Their study determined that the excited state transitions from D_{2h} to C_{2v} , suggesting that only one of the ligands is electronically excited. It was proposed that the symmetry breaking mechanism stems from a displacement in the antisymmetric b_{3u} vibration within the acetylenic unit.⁵² Theoretical work by Batista et al.⁵³ endorsed this description, where a computational study showed that the lowest excited triplet state deforms along a b_{3u} coordinate, breaks the symmetry resulting in the localization of the triplet state on one of the ligands.

The work by Emmert et al.⁵² gave description of the kinetics in the nanosecond regime demonstrating that the symmetry of the lowest excited manifold is already broken.

Stemming from this study the question of whether, at the femtosecond time scale, the initially formed triplet state is delocalized and then localizes.



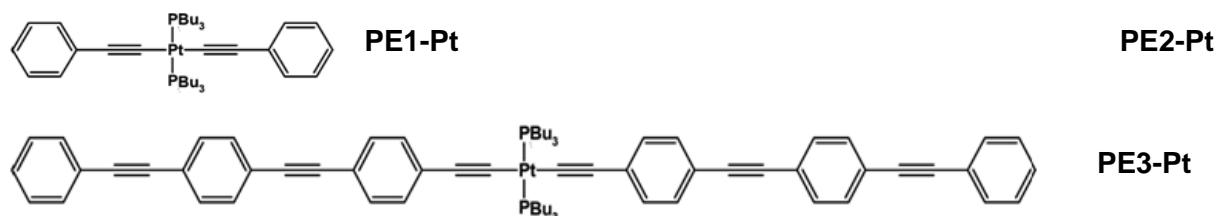


Figure 13: Structures of platinum acetylide complexes.

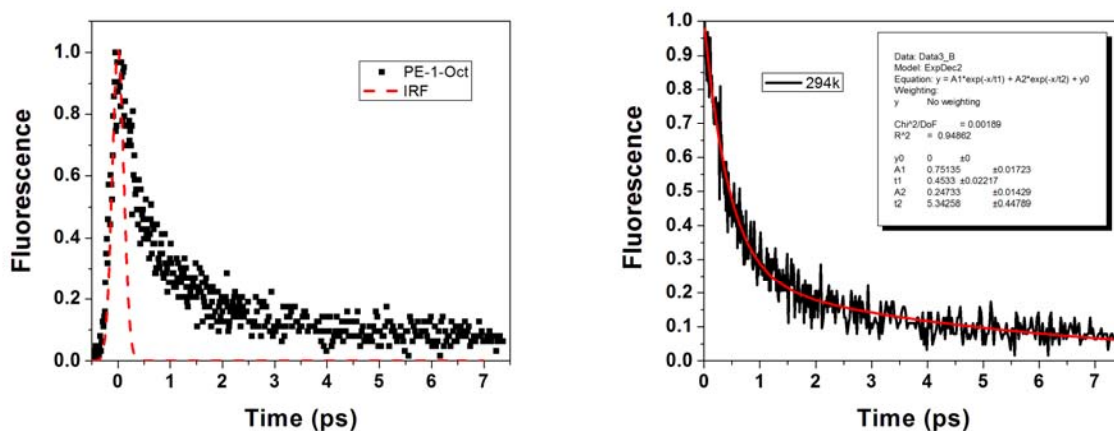


Figure 14: (Left) Time-resolved fluorescence decay at 294k. (Right) Decay fit.

Figure 14 presents the fluorescence decay and exponential decay fit at 294K. The fluorescence decay lifetimes consist of a bi-exponential lifetime of 75% at 453 ± 22 fs and 25% at 5343 ± 448 fs.

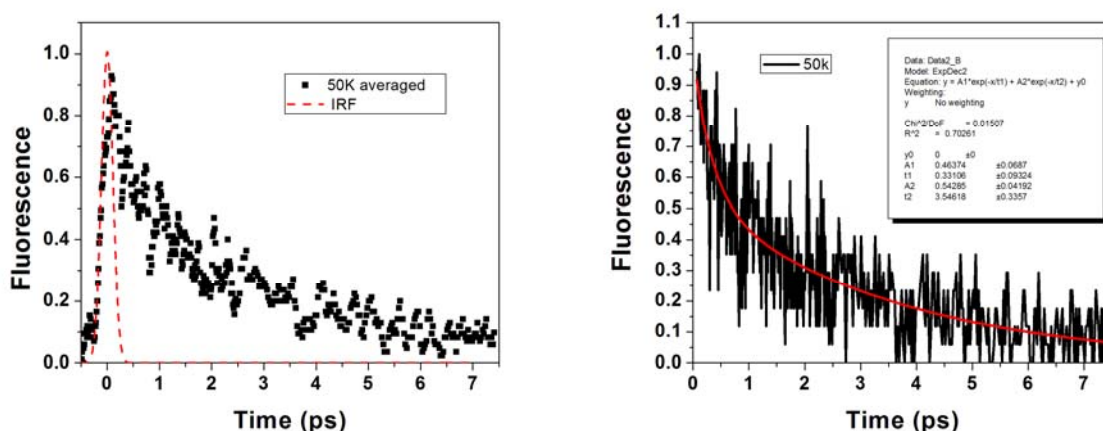


Figure 15: (Left) Time-resolved fluorescence decay at 50k. (Right) Decay fit.

Figure 2 presents the fluorescence decay lifetimes at 50K consist of a bi-exponential lifetime of 46% at 331 ± 93 fs and 54% at 3546 ± 336 fs.

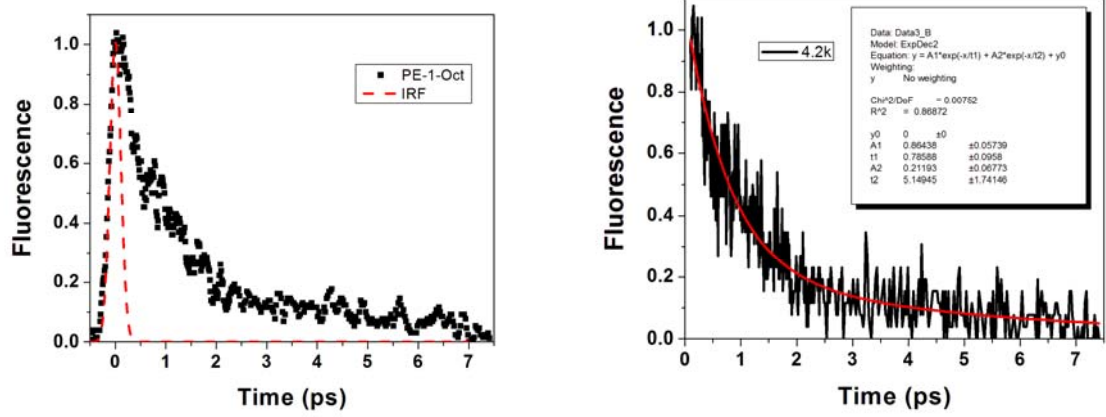
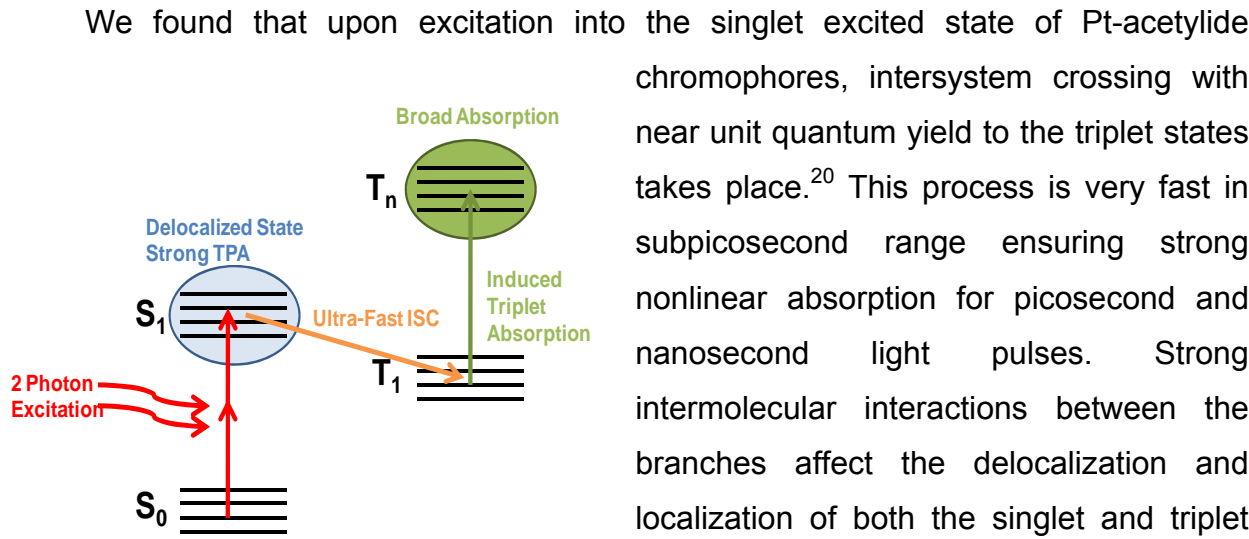


Figure 16: (Left) Time-resolved fluorescence decay at 4.2k. (Right) Fluorescence decay fit.

Figure 16 presents the fluorescence decay fit at 4.2K. The fluorescence decay lifetimes consist of a bi-exponential lifetime of 80% at 786 ± 96 fs and 20% at 5149 ± 1741 fs.

temperature	a1	t1	a2	t2
294K	75%	453 ± 22	25%	5343 ± 448
200K	60%	267 ± 69	40%	6284 ± 1181
50K	46%	331 ± 93	54%	3546 ± 336
4.2K	80%	786 ± 96	20%	5149 ± 1741

Table 1: Bi-exponential decay lifetimes of fluorescence decay.



Scheme1. Nonlinear absorption in Pt-acetylide chromophores

states. The photoinduced absorption spectrum is very broad covering almost entire visible range.²⁰ Singlet absorption red edge has been shown to depend on the chromophore (ligand) length indicating the delocalized character of the singlet state. In order to better understand the fundamental features of the excited state transitions we have performed femtosecond time-resolved fluorescence measurements in wide temperature range 4K-294K.¹⁹ Interestingly we found that the intersystem crossing rate remains very high even at low temperatures (Figure 4, table 1).¹⁹ This indicates a minor involvement of conformational rearrangement in this process as such conformations are expected to be greatly suppressed at low temperatures.

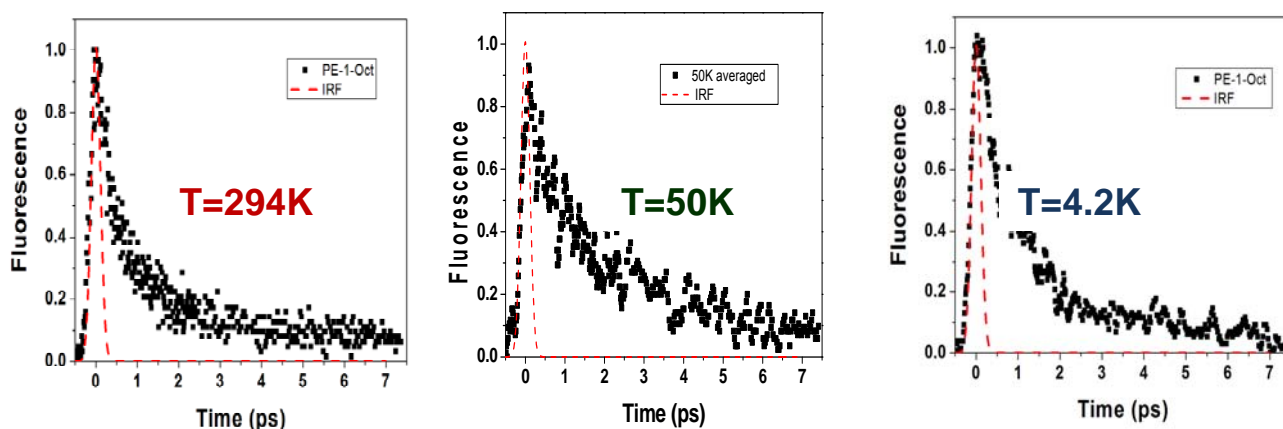


Figure 17. Ultrafast singlet fluorescence decay at 4.2K, 50K as compared to that at room temperature.

The ISC rate independence of the temperature indicates that the conformational changes (which are frozen at low temperature) are not important in ISC process for our system.

This is an important finding in structure-property relationship, which allows for use of larger ligands. Larger ligands support highly delocalized excitations which are very advantageous for the instantaneous TPA.^{1,54} At the same time, the ISC independence of the conformations allows us to use TPA-efficient large ligands without sacrificing ISC rate which is crucial for building up a long-lived triplet-triplet absorption which is of high importance for the optical limiting applications.¹⁹

Fast intersystem crossing leads to broad induced absorption spectrum²⁰ providing the means for nonlinear absorption and optical limiting on subpicosecond time scale

(Scheme 1). Minor involvement of conformational changes paves the way to the development of fast nonlinear systems with large ligands. This is important finding for the structure –property strategy of the systems utilizing ultrafast intersystem crossing for nonlinear optical applications.

Impact:

The intersystem crossing process is very **fast in subpicosecond time scale** ensuring strong **nonlinear absorption** and **optical limiting** in a broad spectral range.

Intersystem crossing (ISC) rate was found to **be independent of the temperature** in a broad temperature rang 4.2-294K indicating minor involvement of conformational change in the process. This is an important finding in structure-property relationship which allows using larger ligands.

Larger ligands support highly delocalized excitations important for **strong** instantaneous **TPA**

The ISC independence of conformations allows for use larger ligands **without sacrificing ISC rate** which is crucial for building up **long-lived triplet-triplet absorption** important for **optical limiting applications**.

Cyclic Ru-Fe and Fe complexes possessing broad absorption extending in near infrared.

Fe(II)-ligand compounds play important roles in various biological systems in which Fe(II)-ligand unit functions at an active site of many important biological processes. Due to their photophysical properties and natural abundance Fe(II)-containing compounds have been suggested for applications light-harvesting photosensitizer materials in solar cell system.

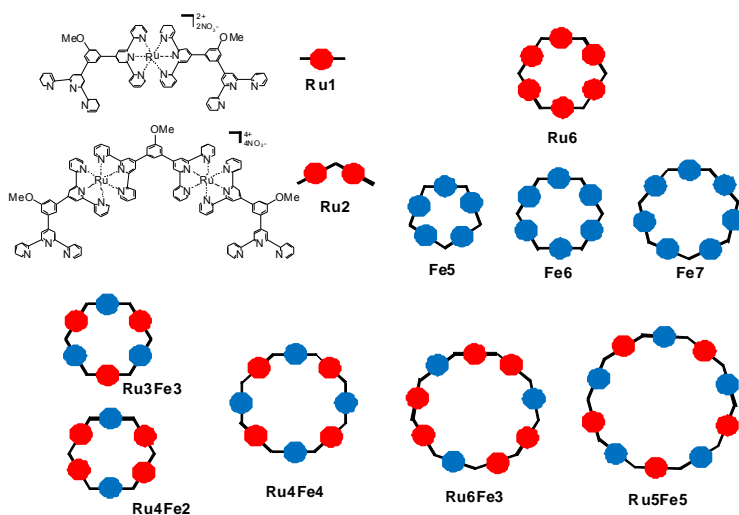


Figure 18. Schematic structure representation of the Ru-Fe and Fe macrocyclic complexes.

Recently synthesized Ru-Fe and Fe cyclic compounds (Figure 18) have broad absorption spectra extending into the near infrared area (Figure 19) and nanocavity which can be potentially used for electron/energy acceptor which is important for many applications.⁸ These new organometallic materials offer flexible broad absorption spectrum control due to different dendron functionalization and fast energy transfer to the metal complex center.

We have performed wavelength-resolved transient absorption as well as steady state spectroscopic measurements in order to study the excited-state charge transfer dynamics in a set of self-assembled cyclic Fe(II)-bisterpyridine compounds with different π -conjugated ligands.⁸

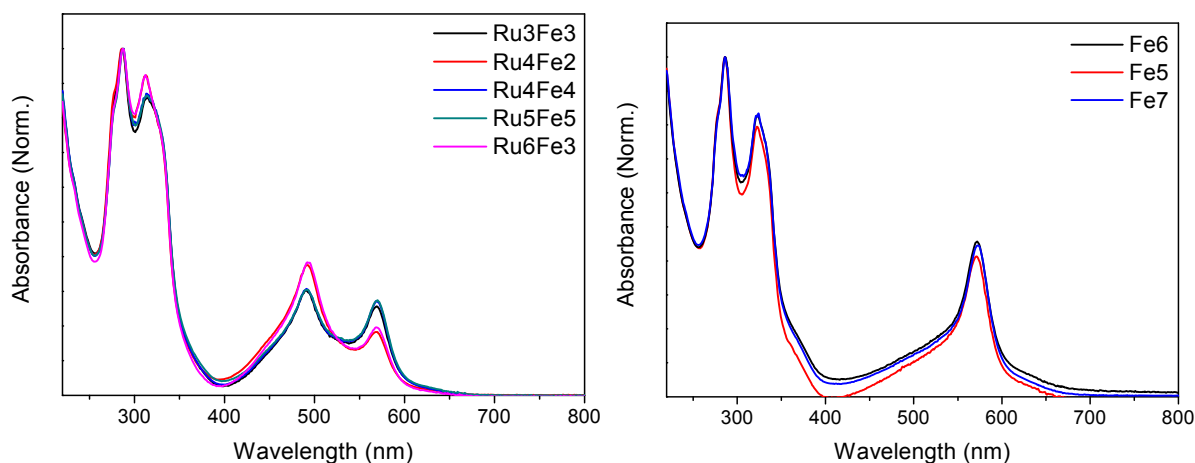


Figure 19. Absorption spectra of the Ru-Fe and Fe macrocyclic complexes.

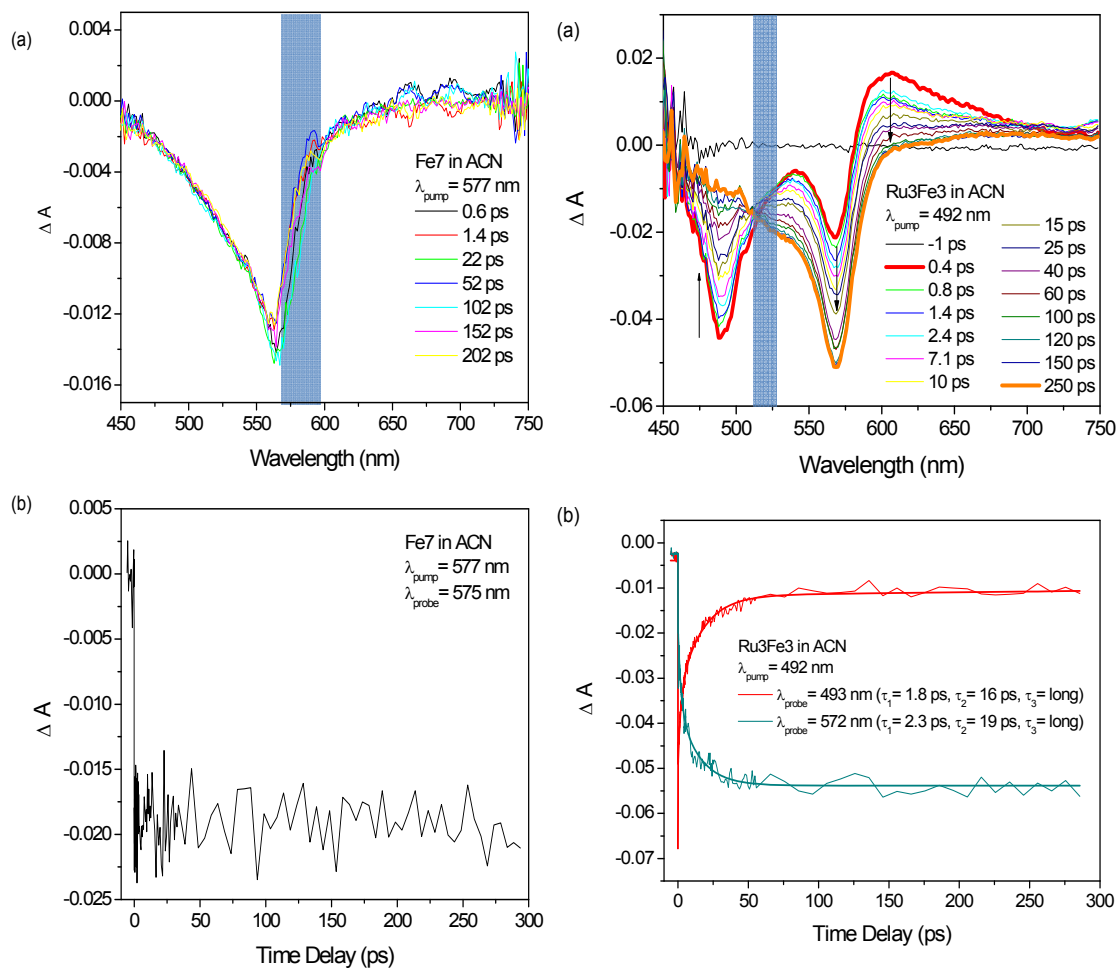


Figure 20. Transient absorption spectra and dynamics demonstrating energy transfer from ligands to the lower-lying metal-to-ligand charge transfer state.

By analyzing multiexponential decay time constants, the internal conversion from ligand-centered π - π^* state to lower-lying metal-to-ligand charge transfer (MLCT) state, followed by the intersystem crossing to the lowest MLCT state was estimated to occur in hundreds of femtosecond time scale. The time constants in range of 7.8 - 10.5 picoseconds were assigned as vibrational cooling processes in lowest MLCT state.⁸ The lowest MLCT state exhibited excited-state lifetimes longer than 5 nanoseconds, indicating the possibility of light-induced excited-state spin trapping (LIESST). In this cascade excited-state energy relaxation processes, the transient spectral shape and decay time constants exhibited analogous features, regardless of the different types of

linkages. The observed excited-state dynamics led us to conclude that the multichromophoric MLCT systems exhibit localized excitation in one chromophore unit, acting like monomeric MLCT systems.⁸

New Fe(II) complexes – based **cyclic light harvesting antenna** is promising for a new generation of thiophene-based efficient photovoltaic systems.

Cyclic complexes possess less **defects** and excitation **traps** due to the rigid ordered structure.

There is a **cavity in nanometer regime** that can be used for the **energy acceptor heterojunction structure** to facilitate exciton dissociation and charge separation for the photovoltaic applications.

Quantum confined silver nanoclusters.

We previously showed that quantum size effects lead to a record high TPA cross-section per one gold atom – 17,000GM.²¹ Thus quantum size effects allow us to fabricate the sample with high nonlinear absorption (optical limiting) using smaller amount of gold at lower cost. Since our early discovery of strong nonlinear properties in gold-dendrimer nanocomposites⁵⁶ we continue investigation of metal nanosized systems for nonlinear optical applications. Silver has the same number of valence electrons but due to the slightly different bonding strength silver nanoclusters showed new feature as compared to gold clusters. They undoubtedly showed magic stable numbers but their structure and abundances were found different from those for gold. Silver quantum sized clusters demonstrated broad absorption, higher (than for gold) extinction, strong fluorescence (Figure 15)⁵⁷

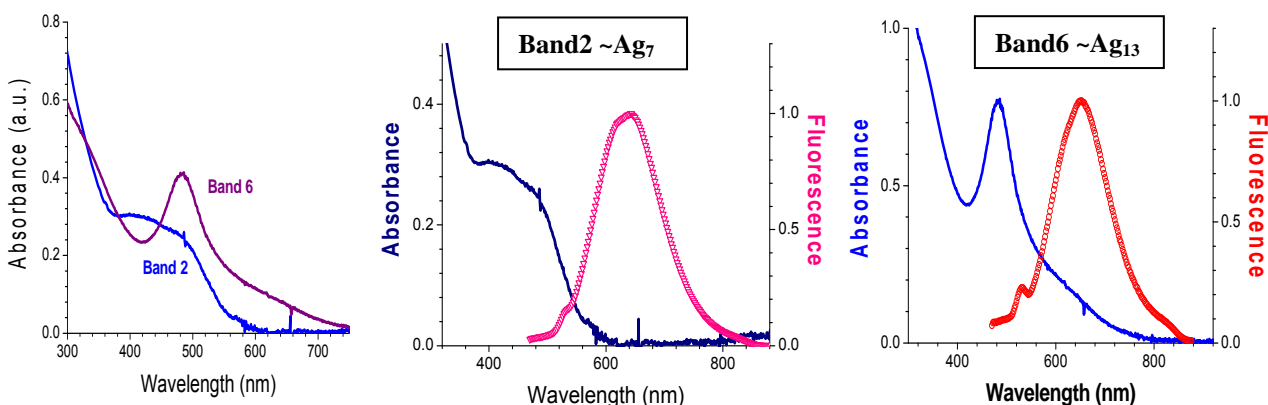


Figure 21. Absorption and emission spectra of quantum- sized silver clusters⁵⁷

Fluorescence of silver clusters was found much stronger than that for gold counterparts. The fluorescence has been observed in both one- and two-photon excitation regimes. This makes these systems very promising for imaging applications. Femtosecond time-resolved transient absorption experiments showed very broad and long-lived excited state absorption feature which can be utilized in optical limiting applications (Figure 22).

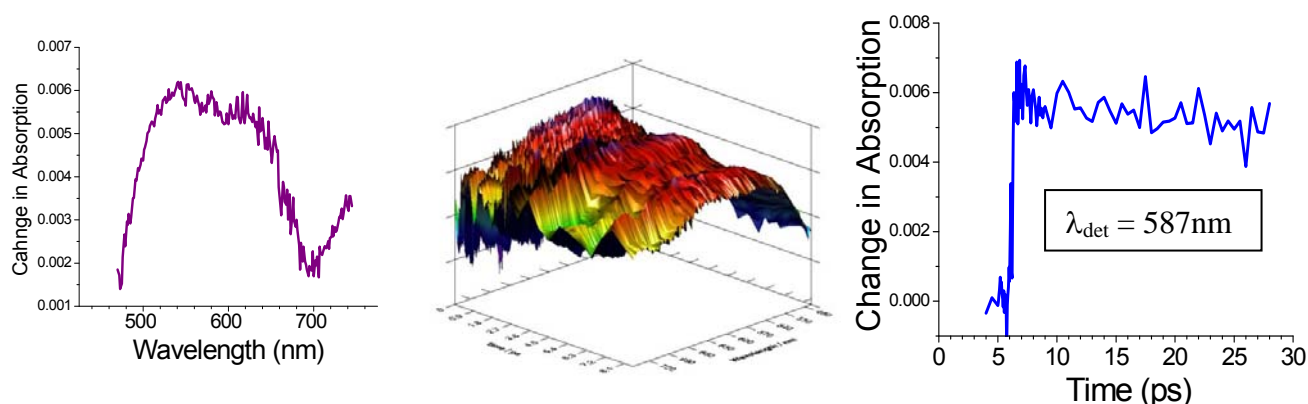
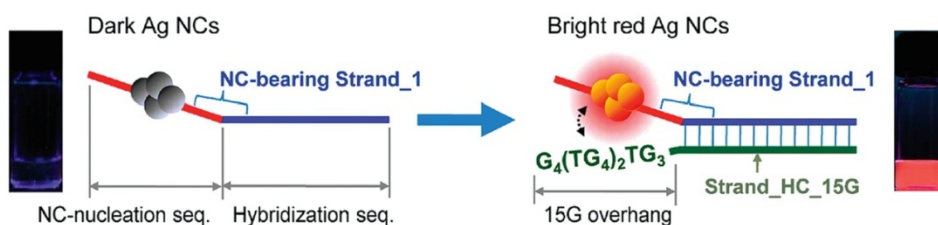


Figure 22. Transient absorption dynamics for silver nanocluster Band2~Ag₇, $\lambda_{exc} = 420\text{nm}$

In collaboration with Dr. J. Martineiz from Los Alamos National Laboratory we have investigated nanosized Ag systems that were bound to DNA sequences.⁵⁸ Ag-DNA probe is smaller than semiconductor quantum dots and more stable than organic dyes.⁵⁹



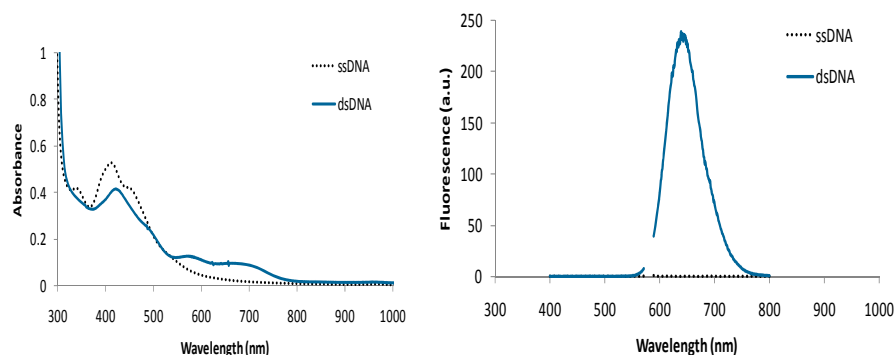


Figure 23. Schematic representation of turn-on fluorescence upon hybridization. Absorption and fluorescence spectra of silver nanoprobe are also shown.

Importantly we have discovered strong two-photon properties for these probes (Figure 24). Quadratic dependence of the fluorescence intensity on the excitation power clearly indicates two-photon efficient two-photon fluorescence.⁵⁸ Two-photon probing allows for better spatial resolution in location of DNA hybridization events and deeper tissue penetration.

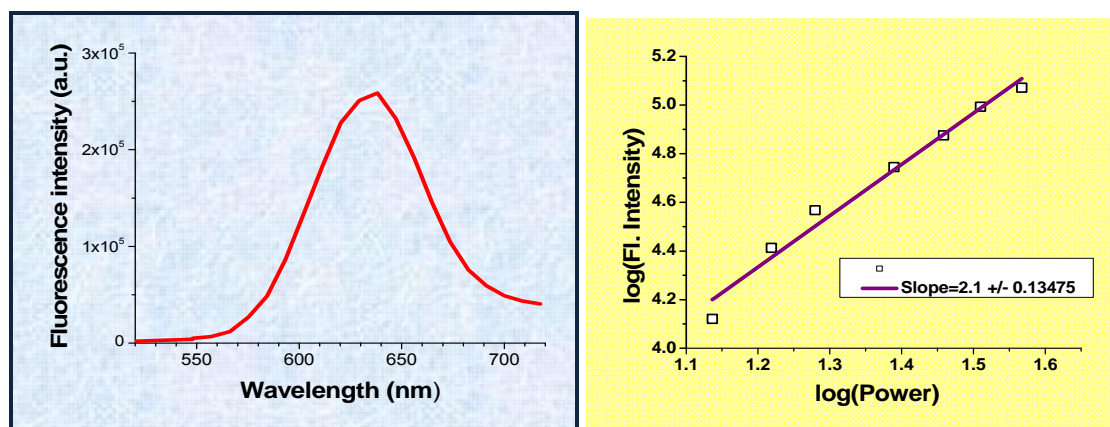


Figure 24. Two-photon excited fluorescence and quadratic dependence of the fluorescence intensity on the excitation power.

Impact:

Silver quantum-sized nanoclusters demonstrate **broad, size controllable absorption spectrum** and strong **two-photon** response.

Our nonlinear and ultrafast spectroscopy results led to better understanding of the fluorescence mechanism in monolayer protected silver clusters to create a **new generation** of **extrabright safe two-photon probes**.

We showed that novel DNA **hybridization indicator** based on DNA –templated silver nanoclusters have **strong two-photon response**.

High two-photon-excited fluorescence efficiency and **low toxicity** make silver quantum-sized nanoclusters very promising for **two-photon-imaging technologies** and bio-applications.

Cubic symmetry nanobuilding blocks: TPA enhancement in 3D – architecture.

Stilbeneoctasilsesquioxanes.

Molecular components assembled in a well defined three-dimensional geometry can potentially lead to novel electronic and nonlinear optical properties. In addition to branched, dendritic, and macrocyclic topologies which showed substantial enhancement of TPA cross-sections over their linear counterparts we have investigated two-photon absorption properties of the donor-acceptor derivatives of stilbenes organized in 3D-cubic geometry around silsesquioxane core.¹⁴

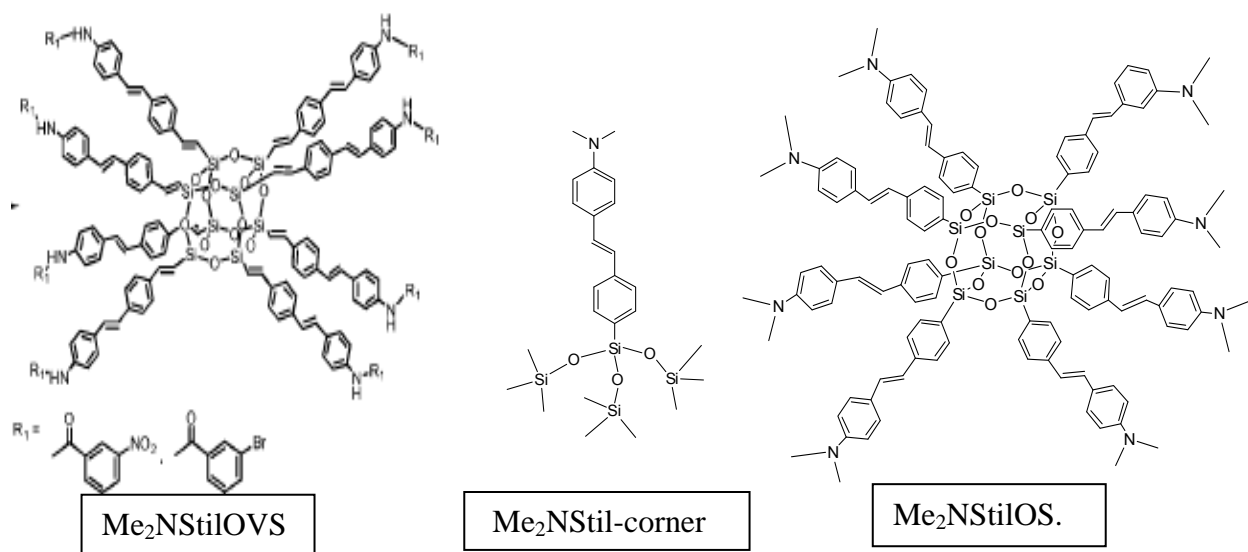


Figure 25. Structures of silsesquioxane cored stilbenes investigated in this work.

The broad emission spectra and low quantum efficiencies of these compounds suggest charge transfer processes occurring in these systems, with Me₂NStil-half having more charge transfer characteristics because its structure includes a larger number of conjugated groups bound together in a smaller volume. In the case of the Me₂N-derivatives, this interaction is primarily a charge transfer interaction as witnessed by the influence of solvent polarity on the emission behavior. The two-photon absorption

behavior is 2-3 times greater on a per *p*-Me₂Nstilbene basis for the full cage than for the corner or half cages. Similar observations were made for *p*-NH₂stilbenevinyl₈OS cages where the greater conjugation lengths led to even greater red-shifts (120 nm) and two-photon absorption cross-sections.²⁵

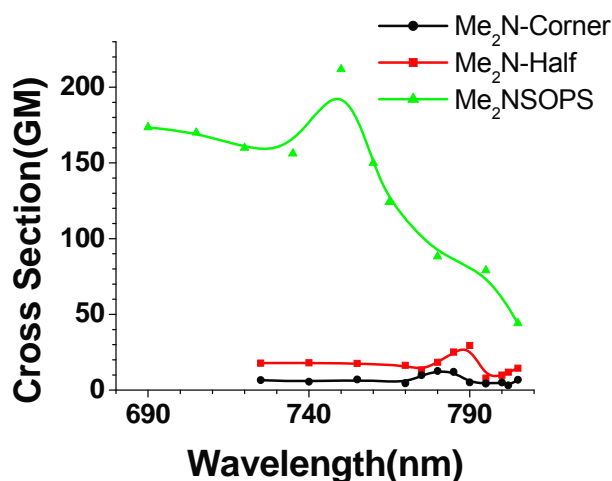


Figure 26. Two-photon absorption cross-section spectra for the investigated chromophores.

Table 2. TPA properties of silsesquioxane derivatives

Sample	δ (GM)	δ /moiety (GM)	λ_{max} nm
MeStil ₈ OS	11	1.2	735
Me ₂ NStil-corner	12	12	780
Me ₂ NStil-half	30	7.5	790
Me ₂ NStil ₈ OS	211	26	755
StilOVS	25	3	705
MeOStilOVS	110	14	705
NH ₂ StilOVS	810	101	720

Perhaps the most important observations from these studies are the fact that the GM value for the full cage is 26/moiety whereas the half cage is 8/moiety and the corner is 12/moiety. The fact that the full cage offers 2-3 times the TPA of the fragments combined with the lowest fluorescence quantum yield suggests that this system offers much higher C-T than the fragments. This type of behavior is more pronounced in the OVS systems studies earlier which have longer conjugation lengths, as seen in the Table 2. However, the data continue to support our contention that in the excited state, the cage seems to influence the photophysics more than would be expected if each corner served solely as an SiO₃ fragment.

Impact:

Ordered 3-D structural organization and strong interchromophore interaction lead to substantial **TPA-response enhancement** over the additive monomers (corners) contributions. These stable molecules with cubic symmetry could be exceptional candidates to for **nanobuilding blocks** to assemble larger regular **very dense mesostructures** possessing strong two-photon absorption capabilities.

These investigations in all have been very useful in discovering new materials and even new applications for the two-photon and optical limiting effects important to the Air Force.

They have helped train more than 5 graduate students and 4 postdoctoral fellows in part. We have published a large number of papers with this previous support and give many lectures and conference presentations with the results obtained from our investigations. We are very grateful for the support of the Air Force in our work.

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